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**by**

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The major research area of this program has been concerned with the fundamental acts of crosslinking polymers by high energy ionizing radiation and the dependence of the crosslinking efficiency and resultant network properties on the state of the system and the temperature at the time the crosslinks are introduced. Besides making the distinction between the crystalline and liquid states it is very important that the effect of the various types of crystallite morphologies also be clearly delineated. The major investigations have been carried out utilizing molecular weight fractions of polyethylene which were crystallized under controlled conditions. This procedure allows the morphology to be described. Irradiations were carried out at different temperatures, and a comparison always made between the crystalline and the completely amorphous polymer. Because of the importance of the crystallite morphology and the segmental motions in these processes concomitant infra-red absorption and broadline nuclear magnetic resonance studies have also been undertaken.

Some of the more recent accomplishments of this research program are embodied in the following manuscripts submitted for publication:

- (1) T. Okada and L. Mandelkern, "Effect of Temperature, Phase and Molecular Weight on the Irradiation of Linear Polyethylene: I. Irradiation in the Completely Molten State", to be presented at the IUPAC Meeting, Japan, 1966.
- (2) T. Okada and L. Mandelkern, "The Effect of Morphology and Degree of Crystallinity on the Infra-red Absorption Spectra of Linear Polyethylene", Accepted by J. Polymer Sci., Part A.

- (3) T. Okada and L. Mandelkern, "The Infra-red Determination of the Degree of Crystallinity of Polyethylene Crystallized from Dilute Solution", submitted to J. Polymer Sci., Part B.

In addition to the above a great deal of emphasis and intensive study has been directed to an investigation of the actual radiochemical reactions that are involved. This has been motivated by our earlier observations, that have been further substantiated, that the relative crosslinking efficiency in the highly crystalline state is about twice as great as in the completely amorphous state at 130°C. In this connection it is important to realize that the usual polyethylene fractions contain one vinyl end-group per molecule. We have found that in the completely molten state at 133°C.,  $G(H_2)$  is inversely dependent on the number average molecular weight while concomitantly the rate of vinyl decay decreases with increasing molecular weight. Hence it appears that the vinyl end-group must act as a hydrogen sink and any analysis of the material balance would be seriously effected. By determining  $G(H_2)$  in the molten state for very high molecular weight polymethylene, for which no vinyl end-groups are detected, the true  $G(H_2)$  value inherent to the polymer and independent of end-group effects was found to be 6.1. It is this value which is important in the quantitative analysis of crosslinking efficiency.

To explain the difference in crosslinking efficiency between the two polymer states a similar constant must be determined for the highly crystalline polymer. Serious complications exist for this case since only the lower molecular weight samples, which unfortunately have high initial vinyl concentrations, yield very high levels of crystallinity. To circumvent this difficulty lower molecular weight samples ( $M_N \approx 15,000$  and  $\approx 50,000$ ) have been hydrogenated, and the infra-red spectra show that the vinyl end-group has been removed. When irradiated in

the completely molten state,  $G(H_2) \approx 6.1$ , as expected, since it corresponds to the asymptotic value previously obtained for the very high molecular weight molten sample. Unexpectedly, the  $G(H_2)$  value for the hydrogenated highly crystalline sample is somewhat lower, hence an apparent anomaly with regard to the crosslinking efficiency would appear to exist. This problem becomes completely resolved however, when the partitioning between sol and gel upon irradiation of the highly crystalline and completely amorphous hydrogenated and unhydrogenated samples are examined. The unhydrogenated samples yield results identical to those previously reported. However, for the hydrogenated samples the results are quite different. Crosslinking in the completely amorphous state is slightly more effective than in the completely crystalline state. We must conclude, therefore, that for the vinyl end-group containing polyethylene in the crystalline state there is an intermolecular crosslinking reaction involving the end groups in which there is no net hydrogen evolution. Detailed kinetic mechanisms are now being developed from the large amount of quantitative data that has been obtained.

Studies are continuing on the broadline nuclear magnetic resonance spectra of molecular weight fractions of polyethylene which have been crystallized under controlled conditions and where the thermodynamic and morphological properties are known from a companion investigation. Sufficient quantitative data for detailed analysis is expected shortly.